

Standard Operating Procedure for the Determination of Total Organic Carbon in Water

1.0 Scope and Application

This method is used to determine total organic carbon (TOC) in water. A concentration of 0.01 mg/L can be measured by some instruments if scrupulous attention is given to minimizing sample contamination and method background.

2.0 Summary of Method

There are two different ways to determine total organic carbon (TOC). The first way is by the TOC mode. The inorganic carbon (IC) is first removed from the sample by acidification and sparging and then the organic carbon (OC) is oxidized to carbon dioxide (CO₂) by sodium persulfate in the presence of ultraviolet light. The CO₂ produced is purged from the sample, dried, and transferred with a carrier gas to a nondispersive infrared (NDIR) analyzer that is specifically tuned to the absorptive wavelength of CO₂. The instrument's microprocessor converts the detector signal to organic carbon concentrations in mg/L based on stored calibration data. The second way is TOC by difference. This is just total carbon (TC) minus inorganic carbon. The TC is all the carbon in the sample, both IC and OC. The IC is determined in the same manner as the in TOC mode.

3.0 Definitions

3.1 The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.2 Liter: L
Milliliter: mL
Grams: g
Total Organic Carbon: TOC
Total Carbon: TC
Inorganic Carbon: IC
Organic Carbon: OC
Carbon Dioxide: CO₂
Non dispersive infrared: NDIR
Dissolved organic carbon: DOC

3.3 May: This action, activity, or procedural step is neither required nor prohibited
May not: This action, activity, or procedural step is prohibited
Must: This action, activity, or procedural step is required

Shall: This action, activity, or procedural step is required

Should: This action, activity, or procedural step is suggested, but not required

4.0 Interferences

- 4.1** Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration, although necessary to eliminate particulate organic matter when only dissolved organic carbon (DOC) is to be determined, can result in loss or gain of DOC, depending on the physical properties of the carbon-containing compounds and adsorption and desorption of the carbon matter on the filter. Avoid contaminated glassware, plastic containers, and rubber tubing. Insufficient acidification will result in incomplete release of CO₂.
- 4.2** The intensity of the ultraviolet light reaching the sample matrix may be reduced by highly turbid samples or with aging of the ultraviolet source, resulting in sluggish or incomplete oxidation. Large organic particles or very large or complex organic molecules such as tannins, lignins, and humic acid may be oxidized slowly because persulfate oxidation is rate-limited. However, oxidation of many large biological molecules such as proteins and monoclonal antibodies proceeds rapidly.
- 4.3** Persulfate oxidation of organic molecules is slowed in samples containing sufficient concentrations of chloride by the preferential oxidation of chloride; at concentrations above 0.05% chloride, oxidation of organic matter may be inhibited. To remove this interference add mercuric nitrate to the persulfate solution in UV-persulfate instruments, or extend reaction time and/or increase amount of persulfate solution in heated persulfate instruments.
- 4.4** With any organic carbon measurement, contamination during sample handling and treatment is a likely source of interference. This is especially true of trace analysis. Take extreme care in sampling, handling and analysis of samples below 1 mg/L TOC.

5.0 Safety

- 5.1** This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals

specified in this method. A reference file of material safety data sheets for each chemical used in this method should be available to all personnel involved in these analyses.

- 5.2 Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.
- 5.3 Unknown samples may contain high concentrations of volatile compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

- 6.1 Tekmar-Dohrman Phoenix 8000 TOC uv-persulfate analyzer or other comparable brand with autosampler.
- 6.2 0-14 pH paper.
- 6.3 10 ml syringe.
- 6.4 0.45 micron glass fiber filters.
- 6.5 125 ml sample bottles:
- 6.6 Autosampler vials: 40 mL amber glass vials with teflon-faced septa. These vials should be washed with laboratory detergent and thoroughly rinsed with tap water followed by reverse osmosis water and allowed to dry. The vials should then be rinsed with acetone followed by hexane and allowed to dry. Finally, the vials should be dried in the drying oven used for drying vials used for the analysis of volatile organic compounds.

7.0 Reagents and Standards

- 7.1 Reagent water: ultrapure from the spectroscopy lab.
- 7.2 21% phosphoric acid: add 37 ml of 85% phosphoric acid to 188 ml of reagent water. Always add acid to water.
- 7.3 LabChem Inc. Catalog number LC12910-1 Organic carbon stock solution. 1000 parts per million. Primary standard grade. 1mL=1mg. If it is prepared in the laboratory, it should be preserved by adding phosphoric acid until the pH is <2. This stock standard solution is used with drinking water samples.
- 7.4 Inorganic carbon stock solution: Dissolve 4.4122 g anhydrous sodium carbonate, in reagent water, add 3.4970 g anhydrous sodium bicarbonate and dilute to 1000 mL; 1mL=1mg carbon. Keep tightly stoppered. Do not acidify. Used for analysis of surface waters in determining TOC by difference. To make the standards use 4 mL to make 20 ppm, 20 mL for 100 ppm, and 40 mL for 200 ppm. There are different methods in the Phoenix 8000 that can be used. Choose the one that best suits the samples involved.
- 7.5 Carrier gas. This lab uses nitrogen, CO₂-free and containing less than 1 ppm hydrocarbon.
- 7.6 Purging gas. Any gas free of CO₂ and hydrocarbons. This lab uses nitrogen.
- 7.7 Persulfate solution. Acros. 98+ %. Add 25 g of sodium persulfate to 213 mL of reagent water and add 9 mL of phosphoric acid.

8.0 Sample Collection, Preservation, and Storage

- 8.1 If possible, rinse bottles with sample before filling.
- 8.2 Collect and store samples in glass bottles protected from sunlight and seal with TFE-backed septa. Preferably use thick silicone rubber-backed TFE septa with open ring caps to produce a positive seal. Before use, wash bottles with laboratory detergent, rinse thoroughly with tap and reverse osmosis water and allow to dry. Then rinse with acetone and hexane and dry in the oven used for drying vials used for analysis of volatile organic carbon compounds. Analyze a bottle blank with each set of sample bottles to determine effectiveness or necessity of cleaning. This can be done by filling a sample bottle (bottle blank) with reagent water in the laboratory when the sample containers are shipped out and holding the sample bottle at 0-4 degrees C until the associated samples are analyzed.

8.3 Drinking water-related samples must either be analyzed or must be acidified to achieve pH <2.0 by addition of minimal phosphoric or sulfuric acid as soon as practical after sampling, not to exceed 24 hours. Check pH before analysis by using a stirring rod to dip in the container and then touch it to the pH paper. If the sample is a groundwater sample, it should not be acidified because there would be a loss of inorganic carbon from the sample in the form of CO₂. Regardless of what is being analyzed, all samples must be stored at 0 - 4 degrees C from the time of collection until analysis.

8.4 All samples must be analyzed within 28 days of the date and time collected.

9.0 Quality Control

9.1 For every set of ten samples, analyze a reagent blank, a known-value check sample, and a duplicate. Analysis of blanks is to show freedom from contamination.

9.2 Analyze a sample bottle blank with each set of samples. See section 8.2 for details.

10.0 Calibration and Standardization

10.1 Use the standard described in section 7.4 for finding TC. If only TOC is to be found, there is a stock solution of organic carbon. The same concentrations can be made up for the organic carbon.

10.2 Depending on whether TC-IC is to be found or TOC is to be found, will determine what curve or curves need to be set active. If just TOC is to be found, then choose SETUP, CALIBRATION, SET ACTIVE, then choose TOC. It will then give ranges of different values. The choice that has been used is 0.1ppm-20ppm for most samples. If TOC is found by way of TC-IC, both curves for TC and IC must be set active. They also must have the same range of calibration. The TOC range should not be set active.

10.3 Once the calibration curve is formed, go to the calibration results. Choose the standards that have just been run and click on the RECALC button. If you want to keep the curve click on OK and then start the run again. The curve is supposed to be linear, so the closer to 1.0000 the better the curve.

11.0 Procedure

11.1 Filtration of drinking water-related samples prior to TOC analysis is not permitted

as this could result in removal of organic carbon. Where turbidity interferes with TOC analysis, samples should be homogenized and, if necessary, diluted with organic-free reagent water.

- 11.2** Bring the analytical batch of samples to room temperature. Make sure the samples are homogenized and pour into labeled amber 40 mL vials. Put on a new septa and place on the rack.
- 11.3** Check the carbonate and bicarbonate levels of the samples to be analyzed. If they are over 800 mg/L then dilute, if necessary.
- 11.4** Make up the reagents weekly. Make up new standards whenever a new run is started.
- 11.5** Warm up the instrument at least one-half hour before use. This means just switch from standby to run, and make sure that the gas flow is 200 cc/min. Make sure the baseline has stabilized.
- 11.6** Create a file and label it according to the current date. An easy way to do this is to load an old file from the setup menu and change the samples that are in it to go along with the new run. Go to the file and use the “save as” and then type in the day of the run. Put the year first then the month and then day. Example: for the date of January 21st, 2002 should be read as 020121.
- 11.7** Set the curve for the desired analysis. The TOC curve should be set for analyzing drinking water-related samples. The TC and IC curve needs to be set active for analysis of TOC by difference. Make sure that all other curves that are not used are not active.
- 11.8** Put the samples on and select run.
- 11.9** The calibration curve should be checked after the first standard is run. This will be sure that the correct calibration is made. The analyst can choose the points on the calibration menu. The more linear the line the better, so if the r-squared number is close to one, and the check sample is in the tolerance limits, let the rest of the samples run.
- 11.10** Only TOC results will be displayed for the drinking water-related samples; whereas, the TOC by difference will be shown as TC, IC, and TOC on the results portion of the screen.

12.0 Data Analysis, Calculations, and Reporting Results

12.1 Calculations

If the instrument does not already do this, calculate corrected instrument response of standards and samples by subtracting the reagent-water blank instrument response vs. TOC concentration. Subtract procedural blank from each sample instrument response and compare to standard curve to determine carbon content. Apply appropriate dilution factor when necessary. Subtract inorganic carbon from total carbon when TOC is determined by difference.

12.2 Reporting Results

The results can be hand entered or electronically transferred to the Laboratory Information Management System (LIMS). The units should be mg/L.

13.0 Method Performance

Interlaboratory studies of persulfate and/or UV with NDIR detection methods have been conducted in the range of 0.1 mg/L to 4,000 mg/L of carbon. The resulting equation for organic carbon single-operator precision is :

$$S_o = 0.04x + 0.1$$

Overall precision is expressed as:

$$S_t = 0.08x + 0.1$$

where:

S_o = single-operator precision
 S_t = overall precision, and
 x = TOC concentration, mg/L

14.0 Pollution Prevention

If mercuric nitrate is used to complex the chloride, use an appropriate disposal method for the treated waste to prevent mercury contamination.

15.0 Waste Management

- 15.1** Disposal of any hazardous waste from this method must be done in accordance with appropriate regulations.
- 15.2** For further information on waste management consult The Waste Management Manual for Laboratory Personnel and Less is Better: Laboratory Chemical Management for Waste Reduction, both available from the American Chemical society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036

16.0 References

- 16.1** Method 5310 C: Total Organic Carbon(TOC), Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method, *Standard Methods for the Examination of Water and Wastewater*, 19th edition supplement, 1996, pp.9-14.
- 16.2** "Dohrman Phoenix 8000 User Manual", 7413 East Kemper Road, Cincinnati, Ohio 45242-9576.
- 16.3** *Federal Register*, Wednesday, December 16, 1998, p 69417.